

Out of equilibrium ion distribution around a suspended particle undergoing electrophoretic motion



Constantino Grosse^{a,b,*}

^a Departamento de Física, Universidad Nacional de Tucumán, Avenida Independencia 1800, 4000 San Miguel de Tucumán, Argentina

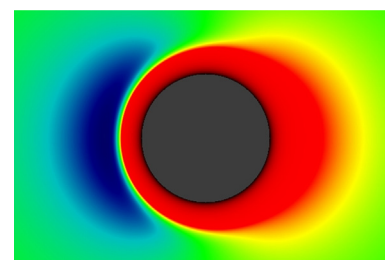
^b Consejo Nacional de Investigaciones Científicas y Técnicas, Avenida Rivadavia 1917, 1033 Buenos Aires, Argentina

HIGHLIGHTS

- The usual representations of the ion densities in electrophoresis are misleading.
- The concentration polarization must be taken into account.
- The counterion density decreases in front and increases behind a moving particle.
- The double layer is slightly thicker in front and thinner behind a moving particle.

GRAPHICAL ABSTRACT

Counterion density around a charged particle moving towards the left in a DC electric field.



ARTICLE INFO

Article history:

Received 6 October 2014

Received in revised form 7 November 2014

Accepted 8 November 2014

Available online 3 December 2014

Keywords:

Ionic atmosphere

Counterion cloud

Diffuse double layer

Concentration polarization

Electrokinetic phenomena

ABSTRACT

It is shown that the often used representations of the ionic atmosphere surrounding a charged spherical particle suspended in an electrolyte solution and moving with electrophoretic velocity under the action of an applied electric field are misleading at best. Numerical results for the actual out of equilibrium counterion, co-ion, total ion, and total charge density distributions are presented.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Ever since the first numerical calculations of the electrophoretic mobility of spherical colloidal particles suspended in aqueous electrolyte solutions [1,2], the surrounding ionic atmosphere perturbed by the applied DC electric field was schematically represented as either the dot or the dash lines in Fig. 1. This

figure and all the forthcoming representations were normalized considering a negatively charged particle in an electric field pointing from left to right so that the particle moves towards the left.

According to Wiersema et al. [1], the dot line in Fig. 1 represents the “ionic atmosphere” while, according to O’Brien and White [2], the dash line represents the “counterion cloud”. This second representation was repeatedly used in later works [3,4] and, according to Ohshima [3], the dash line in Fig. 1 corresponds to the “electrical diffuse double layer”. Finally, a colorful version of this representation resembling a comet (still far away from the sun) was actually adopted as logo for the ELKIN International Symposia on Electrokinetic Phenomena.

* Correspondence to: Departamento de Física, Facultad de Ciencias Exactas y Tecnología, Universidad Nacional de Tucumán, Avenida Independencia 1800, 4000 San Miguel de Tucumán, Argentina. Tel.: +54 381 4364093x7739.

E-mail address: cgrosse@herrera.unt.edu.ar

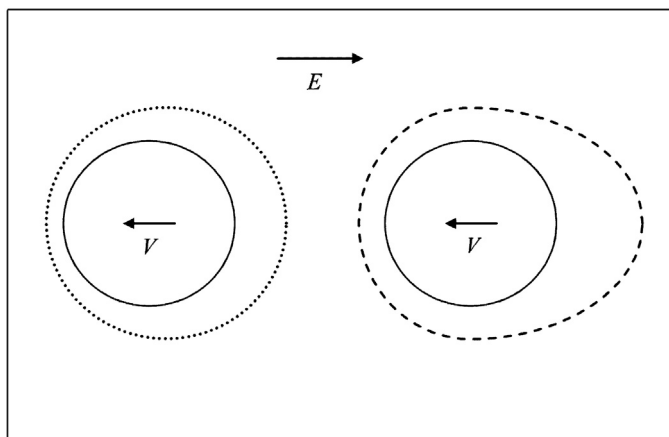


Fig. 1. Two often used schematic representations of a negatively charged suspended particle (solid line) and the surrounding ions (dot and dash lines) undergoing electrophoretic motion (see text). The DC external electric field E is applied from left to right while the electrophoretic velocity V points towards the left.

The motivation for the present work originates in the following apparent contradiction. It is well known from the theory of dielectric and electrokinetic properties of suspensions [5–7] that a DC electric field leads to the appearance of the concentration polarization phenomenon. For a negatively charged particle in an electric field pointing from left to right, the electrolyte concentration increases on the right side of the particle while it decreases on its left side. Therefore, the electric double layer should become thinner on the right side of the particle and thicker on its left side [8,9], so that the particle should move with the thick part of the double layer up front. This qualitative behavior contradicts both representations in Fig. 1.

2. Results and discussion

In order to clarify this contradiction, the ionic concentrations were numerically calculated solving the standard set of electrokinetic equations [10]. The system used was chosen to be both rather typical and such that the electric field induced perturbations were readily visible: a spherical dielectric particle with fixed surface charge (no anomalous surface conductivity) immersed in an aqueous KCl solution such that $\kappa a \approx 10$ and $\zeta = -100$ mV. The system parameters used are given in Table 1.

There are countless numerical works where the equilibrium, $C_0^\pm(r)$, and/or the field induced, $\delta C^\pm(r)$, counterion and co-ion concentrations are represented. However, we are interested here in the total out of equilibrium ion concentrations:

$$C^\pm(r, \theta) = C_0^\pm(r) + \delta C^\pm(r) \cos \theta \quad (1)$$

Table 1
System parameters used in the calculation, Figs. 2–8.

Temperature	298.16 K
Particle concentration	1%
Zeta potential	–100 mV
Solution relative permittivity	78.54
Particle relative permittivity	2.0
Particle radius	100 nm
Electrolyte concentration	0.001 molar
Solution viscosity	0.8904 mP
Diffusion coefficient K^+	$1.9572 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$
Diffusion coefficient Cl^-	$2.0331 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$
Electric field strength	$4.11 \times 10^4 \text{ V m}^{-1}$

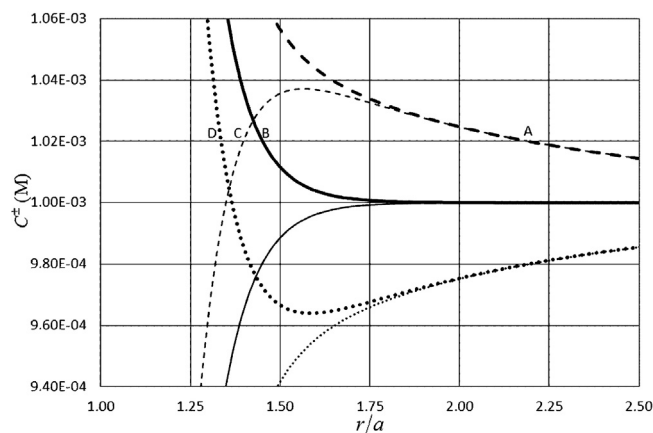


Fig. 2. Counterion (thick lines) and co-ion (thin lines) concentration profiles. Equilibrium for all θ and out of equilibrium on the equator $\theta = \pi/2$ plane (solid lines). Out of equilibrium on the polar axis for $\theta = 0$ (dashed lines) and for $\theta = \pi$ (dotted lines). Characters A–D: see text.

The delicate point to take into account is that the calculated field-induced ion concentrations are linear in the applied field because they are calculated solving the electrokinetic equation set that has been linearized with respect to the applied field strength. Therefore, if the chosen field strength is too weak the obtained results are valid but the effects are hard to appreciate while, if the field is too strong the effects are clearly visible but invalid. The field strength used in the calculation is given in Table 1. This particular value leads to a ratio of the field-induced to equilibrium counterion concentration $\delta C^+(r)/C_0^+(r)$ that is always lower than 5%. It also leads to a potential drop across the particle and its double layer (≈ 10 mV) that is still an order of magnitude lower than the equilibrium potential drop across the double layer (100 mV).

Fig. 2 represents the familiar counterion (thick) and co-ion (thin) equilibrium concentration profiles $C_0^\pm(r)$ (solid lines), which also correspond to the out of equilibrium profiles on the equator plane $C^\pm(r, \pi/2)$ (Eq. (1)). The dashed lines represent the out of equilibrium profiles $C^\pm(r, \theta)$ calculated on the polar axis ($\theta = 0$), while the dotted lines correspond to $\theta = \pi$. The concentration polarization phenomenon: increase (decrease) of the electrolyte concentration on the right (left) hand side of the particle that extends to distances greater than the particle radius can be clearly appreciated. As can be seen, the constant counterion concentration line corresponding to a 2% increment with respect to the bulk intersects the polar axis on the right side of the particle ($\theta = 0$) 120 nm from its surface (point A), crosses the equator plane ($\theta = \pi/2$) 45 nm from the surface (point B), and finally intersects the polar axis on the left side of the particle ($\theta = \pi$) 34 nm from its surface (point D). As for the co-ion concentration, it also increases by 2% on the polar axis ($\theta = 0$) 120 nm from the particle surface (point A). However, the corresponding constant concentration line never crosses the equator plane but rather intersects again the polar axis ($\theta = 0$) 39 nm from the surface (point C).

The spherical coordinates of a generic point (r, θ) belonging to a line of constant ion concentration C , must satisfy the following equation

$$C_0(r) + \delta C(r) \cos \theta = C \quad (2)$$

Therefore, for each calculated r value, its orthogonal coordinates are

$$x = r \cos \theta, \quad y = r \sqrt{1 - \cos^2 \theta} \quad (3)$$

Download English Version:

<https://daneshyari.com/en/article/6979170>

Download Persian Version:

<https://daneshyari.com/article/6979170>

[Daneshyari.com](https://daneshyari.com)